Properties of carbon anode components for aluminium production

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PROFESSIONAL PAPER

The quality of carbon electrode-anode depends on characteristics of coke filler, coal tar pitch binder and anode scrap, which are the components of green anode mixture. Petroleum coke is a dominant component of anode, which finds application in the aluminium production.

The interdependence of physical-chemical properties of the petroleum coke, coal tar pitch binder and anode scrap and their influence on the stability of anode are shown.

The presence of insoluble substances in coal tar pitch exerts a strong influence upon the microstructure and other properties of carbon anode. The connection of the properties and microstructure of anode components and anode quality is discussed.

Key words: petroleum coke, coal tar pitch, anode scrap, carbon anode

1. INTRODUCTION

Aluminium is produced by analytical reduction of alumina (Al_2O_3) through the Hall-Heroult process. Aluminium-oxide is reduced to aluminium by carbon from carbon electrodes, when dissolved in molten cryolite, Na_3AlF_6. The most important property of cryolite is that after heating it turns into melt, one of the rare ones that dissolve aluminium oxide (melting point is 2 000 °C) reducing the temperature to 960 °C.

The electrolysis cell consists of iron tanks lined with insulation material and thick graphite plates (cathode) and carbon electrodes-anodes immersed in cryolite alumina melts.[14] The carbon electrode-anode, in an electrolytic cell for obtaining of aluminium, acts as electrical conductor through which passes the direct current that facilitates the dissolution of alumina. Since the temperature of anodes differs by height, they must have good mechanical properties to avoid breakage and separation of individual parts of anode into the bath.

Components for the production of anodes are petroleum coke (60-70 wt.%), coal tar pitch (14-17 wt.%) and anode scrap (15-20 wt.%).

Since the share of anode costs in aluminium production costs can exceed 20%, control and improvement of its quality are very important, as well as testing of petroleum coke properties, which considerably affect the quality of anode.

The quality and application of petroleum coke depends on the properties of feed stocks, i.e. oil (such as density, content of aromatics, asphaltenes, sulphur, metal ingredients, Conradson carbon) and the coking process conditions (temperature, pressure, time, recycling ratio, process type, capacity, equipment, kinds and ratios of feedstock components, etc.). Each day this valuable refinery product finds more and more applications, most frequently in ferrous and non-ferrous metallurgy, chemical industry and mechanical engineering.

The calcined petroleum coke, obtained by carbonization of heavy oil fractions and oil residue, is used as filler in the production of carbon anodes. Petroleum coke must be of optimum density, ensuring sufficient porosity for interaction with the binder, good electrical conductivity and appropriate strength. Above properties are important to ensure anode thermal characteristics and stability during the electrolysis process. Low content of metal admixtures and sulphur in coke are required for lower anode reactivity, i.e. lower anode material consumption and lower aluminium pollution.[4,5] These properties depend on anode production process and on coke composition and microstructure.

Coal tar pitch is obtained as a by-product of coal pyrolysis and is a complex mixture of hydrocarbon compounds. It is mainly used as a binder in the production of electrodes in ferrous and non-ferrous metallurgy, but can be a component of carbon fibers, C-C composites and lubricant up to 400 °C.[9] Coal tart pitch binds the coke particles by entering the pores and filling the cavities between them. Viscosity, penetration ability and chemical reactivity define the good binding properties of a coal tar pitch.[11] Chemical composition of coal tar pitch is an exceptionally important parameter of anode quality, and so is the share of aromatic hydrocarbons, which accelerate thermal polycondensation resulting in the formation of high-molecular compounds in the structure of anode material. The most frequent coal tar pitch characterization method is the analysis of group composition of coal tar pitch fractions, based on partition of pitches according to solubility of their compounds in organic solvents. On that basis we can distinguish between[15]:

α-fraction of resin or quinoline – insolubles (KNT) known in two main forms:

α_1-fraction or primaray fraction, formed by cracking of volatile components and their separation at high temperatures in the process of coal distillation;

α_2-fraction or secondary fraction, formed by polymerization of initially present α_1-fractions at increased temperatures.

β-fraction of resin is the difference between toluene – insolubles (TNT) and quinoline – insolubles (KNT) matter. That fraction slightly changes up to 460 °C, but its ratio considerably increases above this temperature, particularly after resin ageing.

Anode scrap can be green and baked. Green anode scrap is created after rejection of the first anode mass until the appropriate mass temperature is reached. In the electrolysis process, when replacing anodes from time to time, the appearance of unused portions of the anodes as baked anode scrap is unavoidable. It can also be created after damage of baked anodes in transportation or from rejected waste. After thorough cleaning, about 20% of anode scrap represents recycling material whose properties affect the quality of finished anodes.[3]

Anodes for the production of aluminium can be green or baked (Soederberg) electrodes. Baked anodes are produced by thermal processing at 1 150 °C and they contain less binder material. A green mixture which contains 60-70 wt.% of petroleum coke and 30-35 wt.% of coal tar pitch is used for preparation of Soederberg anode, and "baking" is conducted under working conditions, i.e. when they reach the electrolysis cell.[6]

2. EXPERIMENTAL PART

In experimental part were investigated physical-chemical properties of petroleum coke as filler, coal tar pitch as binder, anode scrap and the carbon electrode – the anode itself. Investigation was also conducted regarding the microstructure of petroleum coke, anode scrap and anode.

The calcined regular grade petroleum coke was produced by coking of the feedstock composed of atmospheric residue, pyrolysis residue and decanted oil.

The samples were ground to the required particle size in an electrical mill.

Determination of ash content

The ash content was determined by first drying the samples at 110 °C to constant mass and then ashing them for 1 hour at 500 °C, followed by 2 hours at 750 °C and at 950 °C to constant ash mass.

Determination of metal and non-metal content

For metal content analysis ash samples were converted into a solution using the wet oxidation method in an autoclave. Concentrated HNO_3 was used for oxidation for 5 hours at 200 °C.

The metal content was determined by atomic absorption spectrometry method in an aliquot part of the prepared solutions with corresponding blind tests.

The sulphur and carbon content was determined by burning in an oxygen flow in a Leco analyser.

Coal tar pitch sample analyses

The content of aromatic and asphaltene compounds was determined employing the modified liquid chromatographic technique according to ASTM 2007-75.

The content of α fraction in coal tar pitch was determined using the H. Marsh at all[8] method based on dissolution of coal tar pitch in warm quinoline (75 °C). The obtained mixture was filtered and undissolved part washed with toluene and acetone, i.e. benzene and acetone. The content of β fraction was calculated from the ratio of toluene insolubles (w_{TNT}) and ratio of quinoline insolubles (w_{KNT}) according to the expression: $w_\beta = (w_{TNT} - w_{KNT}) / (1 - w_{KNT})$. Toluene insolubles were determined by dissolution of 100 mg of coal tar pitch in 2 ml of solvent at 200 °C. The sample was centrifuged after 24 hours, followed by decanting of solvent, and the procedure was repeated until the solvent became colourless.

Determination of density

The density of samples was determined applying the standard ISO 3 675 method.

Determination of microstructure

Microstructure of samples was determined by optical microscopy. Previously prepared 10 mm sample was used for analysis. The preparation process included grinding and polishing. The sample was ground and polished under tap water using the „Vector LC" (Buehler) automatic sample preparation unit. The 600 grit size sand paper was used for grinding and Microcloth containing alumina aqueous suspension of 0.3 μm granulation was used in the polishing phase. After polishing, the sample was rinsed with water and alcohol and dried by hot air.

Microstructure was analysed by the „Olympus GX 51"optical microscope with DP 70 digital camera. Microstructure was observed under polarized light.

3. RESULTS AND DISCUSSION

Components of carbon electrode – anode intended for electrolytic production of aluminium, were tested. Bearing in mind that petroleum coke is a dominant anode mass component, its properties and microstructure considerably contribute to the quality of baked anodes. Overconsumption of anodes in the form of reactivity towards O_2 and CO_2 is under the influence of present metals and sulphur („purity"), anode structure and porosity.[7] It is well known that higher content of ash, i.e. metals, alkali ones in particular, in the anode mass contributes to higher anode reactivity. Metals (especially sodium, vanadium and cobalt) act as catalysts in oxidation of carbon during the electrolysis process. According to the results shown in Tables 1 and 2, anode scrap has the highest ash content (0.41 wt. %) and coal tar pitch the lowest (0.14 wt.%), which is understandable in view of the origin of these anode mass components. Namely, anode scrap obtained from electrolytic cell is partially covered with alumina and hardened bath material, which contain the major part of metal admixtures.

Table 1. Results of investigation of petroleum coke, anode scrap and anode properties

PROPERTIES	PETROLEUM COKE	ANODE SCRAP	ANODE
Real density, kgm^{-3}	2 062	2 039	2 048
Carbon, wt.%	88.5	90.2	91.2
Sulphur, wt.%	1.62	1.81	1.68
Ash, wt.%	0.24	0.41	0.29
Sodium, $mgkg^{-1}$	58.2	111.3	84.1
Vanadium, $mgkg^{-1}$	20.2	34.8	32.1

Table 2. Properties of coal tar pitch

COAL TAR PITCH	
CONTENT	
Mass loss, wt.%	21.2
Ash, wt.%	0.14
Metals, mgkg^{-1}	
Ca	140.1
Na	160.2
V	18.2
Sulphur, wt.%	0.43
Aromatics, wt.%	91.2
Asphaltenes, wt.%	1.3
Fraction composition, %	
α_1- fraction	8.8
α_2- fraction (450 °C)	52.4
β- fraction	28.1

The investigated coal tar pitch contains less vanadium (18.2 mgkg^{-3}), and more sodium (160.2 mgkg^{-3}) and calcium (140.1 mgkg^{-3}). The properties of baked anodes are particularly affected by the sodium present in coal tar pitch.[1] Increased sodium content in coal tar pitch has an influence on faster air oxidation of anodes, but does not affect anode density and strength. Reactivity of coal tar pitch plays a significant role in the production of anodes. It is important that during the baking process the binder pitch liquid quickly converts into solid carbon phase of binder „bridges“.[2]

One of the main criteria that determine the use of coal tar pitch as binder in anode production is the α-fraction content.[13] That fraction has an effect on carbonization processes and product structure. Higher ratio of α_1-fraction indicates increased aromatic compound content and relatively low pitch softening temperature, necessary for its binding properties. However, higher content of that fraction reduces the wetting ability (caking capacity) and some other properties. With that in mind, the α_1-fraction content is limited to 16%.[8] Increase of temperature results in secondary, α_2-fraction, which acts as a centre of nucleation in the carbonization process, ensuring the creation of well graphitized secondary carbon which is a result of binder carbonization. According to the obtained results (Table 2) the tested coal tar pitch has a satisfactory composition of these fractions (α_1-fraction = 8.8%, α_2-fraction = 52.4%).

Anode microstructure is associated with its consumption during electrolysis. Petroleum coke, used as filler, will contribute to lower anode reactivity providing its microstructure has a well organized distribution of crystallite, contributing to the increase of real density and anode compaction. Figure 1 shows the microstructure of petroleum coke obtained by observation under a polarized light. Presence of both micro structural elements, lamellae and mosaic, is visible. However, presence of fine and medium mosaic areas is somewhat more pronounced. Figure 3 shows the microstructure of anode which is similar to the microstructure of petroleum coke, but bonding of filler and binder in the form of lamellar elements is evident. Places where pores are partially filled with binding coal tar pitch are visible. As expected, the microstructure of anode scrap (Figure 2) is very similar to anode microstructure.

β-fraction is important for the creation of mesophase as a product of polycondensation processes, which are the basis for coke skeleton forming. However, excessive presence of â-fraction is not desirable, since it is associated with higher ratio of lamellae which will not result in good bonding of coke grains and will have an impact on its higher reactivity and faster anode consumption.[15] The content of β-fraction is therefore limited to 35% and the tested coal tar pitch has a satisfactory content of this fraction.

Accordingly, to anticipate the anode quality on the basis of individual component properties it is necessary to test each mixture entering the production process.

Sulphur in coal tar pitches has different ratios and comes in different forms depending on the kind of coking feed and coking conditions. It can be thermally stable or instable. Under the influence of heat, particularly above 1 000 °C, thermally unstable sulphur is separated and coke porosity increases.[12]

Increased sulphur content in coke can lead to anode „puffing“. The cokes that „puff“ are more porous and prone to oxidation and have lower density and strength. Table 1 shows that analysed samples of anode components have acceptable sulphur content values (max. 1.81 wt.%), and it can be assumed that effect of temperature during anode baking and electrolysis would not cause significant changes due to the effect of „puffing“. Some metals (for example vanadium, nickel), if present at the same time with sulphur, catalytically affect thermal polycondensation of pitches, resulting in the higher ratio β-fraction.[10]

4. CONCLUSION

In addition to knowledge of physical-chemical properties of petroleum coke as the dominant component in the production of high-quality carbon electrode-anode knowledge of petroleum coke microstructure, and sulphur and metal content in particular, is also required. The obtained results have indicated that if the coke does not contain too much sodium and vanadium and thermally unstable sulphur and has an appropriate share of lamellae in its microstructure, good binding efficiency between petroleum coke and coal tar pitch as binder can be achieved by baking the anode mass. Anodes produced from such components will be less reactive to CO_2 and their consumption rate during electrolysis will be lower.

The results of investigation of group composition of fractions, based on solubility in organic solvents, points to the satisfactory quality of the tested binder pitch. Low sulphur and metal content (calcium, vanadium and sodium in particular) contributes to good characteristics of the tested coal tar pitch. It is confirmed by the ratio of α and β fractions, which have an impact on chemical and structural changes of the binding coal tar pitch at higher temperatures.

When preparing the green anode mass, particular attention should be paid to thorough cleaning of anode

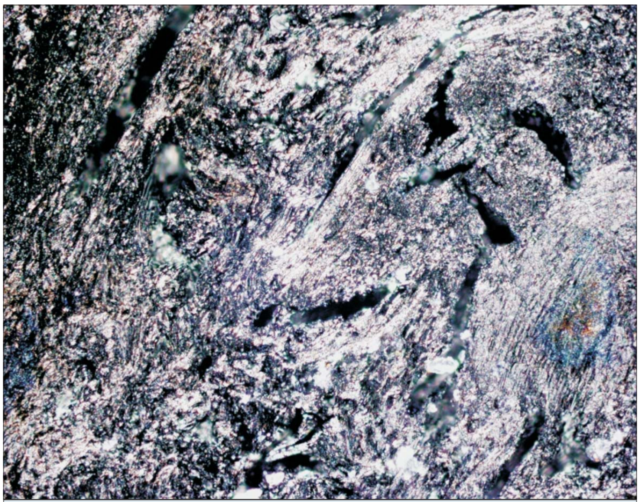

Fig. 1. Optical micrograph of petroleum coke microstructure (polarized light); magnification 200x.
Sl. 1. Optička mikrografija mikrostrukture naftnog koksa pod polariziranim svijetlom; povećanje 200x.

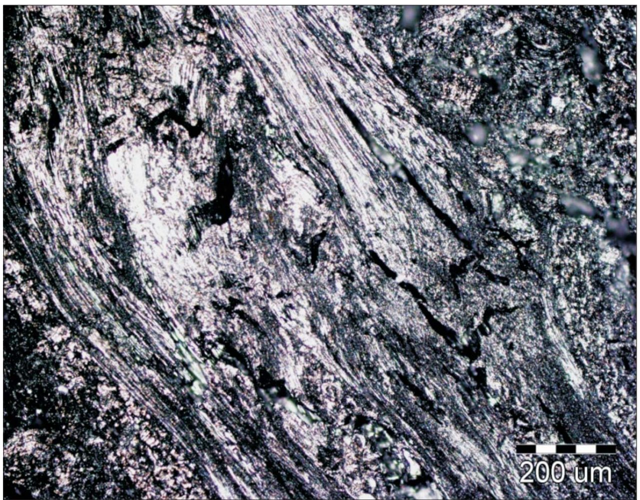

Fig. 2. Optical micrograph of anode scrap microstructure (polarized light); magnification 200x.
Sl. 2. Optička mikrografija mikrostrukture anodnog ostatka pod polariziranim svijetlom; povećanje 200x.

scrap or it will contribute to increased share of impurities (ash, metals) in the baked anode.

Dependence between properties and mictrostructure of carbon anode components and its quality is complex and requires continuous monitoring under operating conditions.

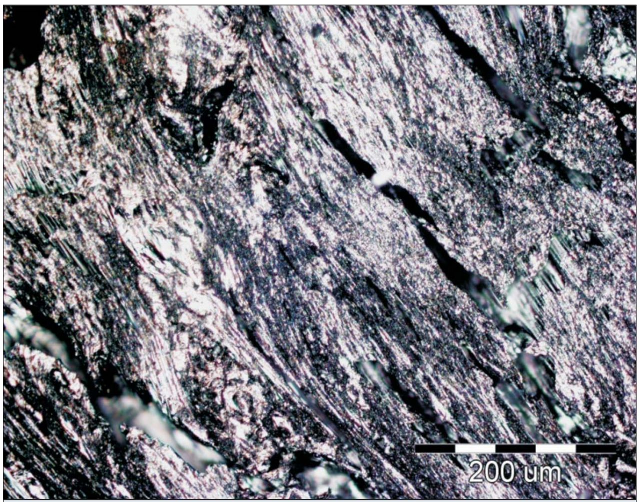

Fig. 3. Optical micrograph of anode microstructure (polarized light); magnification 200x.
Sl. 3. Optička mikrografija mikrostrukture anode pod polariziranim svijetlom; povećanje 200x.

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